Translation

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference K927-PCT	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. PCT/JP02/13813	International filing date (*day/month/year*) 27 December 2002 (27.12.02)	Priority date (*day/month/year*) 27 December 2001 (27.12.01)
International Patent Classification (IPC) or national classification and IPC C03C 27/10, H01L 21/304, B08B 7/00, G02B 1/10		
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1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 3 sheets, including this cover sheet.

☒ This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 11 sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☐ Certain observations on the international application

Date of submission of the demand	Date of completion of this report
06 August 2003 (06.08.03)	22 August 2003 (22.08.2003)
Name and mailing address of the IPEA/JP	Authorized officer
Facsimile No.	Telephone No.

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.
PCT/JP02/13813

I. Basis of the report

1. With regard to the **elements** of the international application:*

☐ the international application as originally filed

☒ the description:

pages 1,4,10,11, as originally filed
pages 2,3,3/1,5,5/1,6,7,7/1,8,9, filed with the demand
pages _____, filed with the letter of _____

☒ the claims:

pages _____, as originally filed
pages _____, as amended (together with any statement under Article 19
pages 1-3, filed with the demand
pages _____, filed with the letter of _____

☒ the drawings:

pages 1-4, as originally filed
pages _____, filed with the demand
pages _____, filed with the letter of _____

☐ the sequence listing part of the description:

pages _____, as originally filed
pages _____, filed with the demand
pages _____, filed with the letter of _____

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.
These elements were available or furnished to this Authority in the following language _____ which is:

☐ the language of a translation furnished for the purposes of international search (under Rule 23.1(b)).
☐ the language of publication of the international application (under Rule 48.3(b)).
☐ the language of the translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

☐ contained in the international application in written form.
☐ filed together with the international application in computer readable form.
☐ furnished subsequently to this Authority in written form.
☐ furnished subsequently to this Authority in computer readable form.
☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. ☐ The amendments have resulted in the cancellation of:

☐ the description, pages _____
☐ the claims, Nos. _____
☐ the drawings, sheets/fig _____

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).**

* *Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rule 70.16 and 70.17).*

** *Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.*

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Claims	1-3	YES
	Claims		NO
Inventive step (IS)	Claims	1-3	YES
	Claims		NO
Industrial applicability (IA)	Claims	1-3	YES
	Claims		NO

2. Citations and explanations

Documents cited in the ISR:

1. JP, 10-282339, A (DIRECTOR GENERAL, AGENCY OF INDUSTRIAL SCIENCE AND TECHNOLOGY), 23 October 1998
2. JP, 10-282499, A (DIRECTOR GENERAL, AGENCY OF INDUSTRIAL SCIENCE AND TECHNOLOGY), 23 October 1998
3. JP, 5-251415, A (HAMAMATSU PHOTONICS K.K.), 28 September 1993

Documents 1 and 2 respectively describe a method for adhering transparent substances such as silica glass by interposing an alkoxide such as tetramethoxysilane between two substances made of a material (at least one of which is transparent to ultraviolet light), and adhering the two substances by irradiating the alkoxide portion with ultraviolet light.

Document 3 describes using a quartz glass plate transparent to ultraviolet light in a window between a light source part and a cleaning chamber in a light cleaning apparatus, and describes using a light-emitting window.

Documents 1 through 3 neither describe nor suggest the point about using mechanical pressure from the outside to reduce irregularities in the gaps between the aforesaid two substances and to improve adhesion, and irradiating the alkoxide portion with ultraviolet light whose wavelength is shorter than 200 nm. It is not something that a person skilled in the art of the relevant technical field could obviously or theoretically arrive at.

index, reduction of planarity and the like of the materials in the adhered portion.

Under these circumstances in conventional techniques, an object of the present invention is to provide a simple and high-quality adhering method capable of ensuring transmission of ultraviolet light at ever-shorter wavelengths.

As related arts, a technique of vitrifying an alkoxide into a thin film by ultraviolet light excitation is known and this technique is disclosed, for example, in Applied Physics Letter, Vol. 69, No. 4, pages 482 - 484 (1996), and Japanese Unexamined Patent Publication (Kokai) Nos. 10-282339 and 10-282499. These Kokai Nos. 10-282339 and 10-282499 are an applied invention of the adhesion technique described in Applied Physics Letter, Vol. 69, No. 4, pages 482 - 484 (1996) and in all of these techniques, an ultraviolet ray is irradiated on a substrate (first step), an adhesive solution is coated on the UV-irradiated portion and an ultraviolet ray is again irradiated thereon to perform the synthesis of SiO_2 (second step), thereby attaining adhesion.

The present inventors have further continued studies on the adhesion technique using an alkoxide and found that the adhesion can be attained only by the irradiation of an ultraviolet ray after the coating of the adhesive solution, and this finding leads to the accomplishment of the present invention.

Japanese Patent No. 2901963 states that this method of forming a thin film by light excitation using an alkoxide as a starting material can be applied to, for example, formation of an antireflective film on the cathode ray tube surface of a television, doping of a functional organic material, production of a photocatalyst, formation of a fine pattern film or formation of a photosensitive material or the like into a thin film.

However, these related arts are not concerned with a

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simple and high-quality adhering method capable of ensuring transmission of ultraviolet light at short wavelengths.

Also, a photo-cleaning apparatus using a quartz glass plate for the ultraviolet light-transmitting window is known (see, for example, Kokai No. 5-251415). However, the existing quartz glass plate is restricted in the size and the large-sizing of the apparatus is limited.

DISCLOSURE OF THE INVENTION

The present inventors have made intensive investigations to achieve the above-described object and confirmed that when at least one material is transparent to ultraviolet light, the materials can be adhered by using an alkoxide as an adhesive and irradiating ultraviolet light under certain conditions and, moreover, the adhered portion is transparent to ultraviolet light. As a result thereof, the present inventors have succeeded in developing a high-quality adhering method ensuring transparency to ultraviolet light and capable of being easily and simply performed at room temperature, in producing a large-area quartz glass plate adhered by using the method. That is, according to the present invention, the following inventions are provided.

(1) A method for adhering a transparent material, comprising interposing an alkoxide between two materials, at least one of which comprises a medium transparent to ultraviolet light, externally applying a mechanical pressure to said two materials so as to reduce uneven gaps and improve contact between said two materials, using a nitrogen or rare earth gas atmosphere in order to prevent ultraviolet absorption, and irradiating ultraviolet light with a wavelength shorter than 200 nm to the above alkoxide portion, thereby adhering those two materials.

(2) An adhered quartz glass plate comprising two or

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more quartz glass plates laterally adhered in accordance with the adhering method as recited in (1) above to provide a larger area, with the adhered part being transparent to ultraviolet light at a wavelength shorter than 350 nm.

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(3) A photo-cleaning apparatus comprising a light source part having one or a plurality of excimer lamp(s) or low-pressure mercury lamp(s), by which ultraviolet light is irradiated from said light source to an article to be cleaned disposed in a cleaning chamber, characterized in that the adhered quartz glass plate as recited in (2) above is used for a window between the light source part and the cleaning chamber.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a view showing the shape of a glass plate.

Fig. 2 is a view showing the state where ultraviolet light is irradiated on a glass plate from a light source.

Figs. 3A to 3F each is a view showing another embodiment of the method for adhering glasses of the present invention.

Fig. 4 is a view showing an embodiment of the photo-cleaning apparatus using an adhered quartz glass plate for the window.

Fig. 5 is a view showing a working example of a photo-cleaning apparatus.

MODE FOR CARRYING OUT THE INVENTION

The method for adhering UV-transparent materials of the present invention has an object of adhering two materials with at least one material comprising a medium transparent to ultraviolet light. More exactly, the object is to provide an adhering method of adhering a medium transparent to ultraviolet light and giving an adhered part still transparent to ultraviolet light.

A representative medium transparent to ultraviolet light is quartz glass but the present invention is not limited thereto. The quartz glass transmits light even down to a wavelength of about 160 nm. Incidentally,

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common glass transmits only light down to a wavelength in the vicinity of 370 nm and does not come under the UV-transparent material as referred to in the present invention. The method of the present invention cannot be used and is not intended to use for such a material having no transparency to ultraviolet light. However, even if the material is not entirely composed of a UV-transparent medium, when the adhesion peripheral part is composed of a UV-transparent medium, the present invention can be of course applied.

At least one of two materials adhered by the method of the present invention must be transparent to ultraviolet light but another material is not limited to a UV-transparent material. Accordingly, the another material may be any of common glass, other glasses and various inorganic solid dielectric materials, metals, semiconductors and organic materials, such as copper plate, silicon plate, plastic plate and protein thin film.

As described above, the present invention is characterized in that materials with at least one being a UV-transparent material are adhered by using an alkoxide as the adhesive and irradiating ultraviolet light.

The present inventors have found and confirmed that the alkoxide decomposes by absorbing ultraviolet light and acts as a kind of adhesive to form bonding with glass or other inorganic or organic solid material and after the formation of adhesion, the alkoxide transmits ultraviolet light. In general, the alkoxide is presumed to be vitrified after the irradiation of ultraviolet light.

Although it is not intended to be limit the present invention by the theory, the reason why the alkoxide exhibits an adhesive activity is considered as follows. The alkoxide particularly useful for glasses is a silicon alkoxide and when a silicon alkoxide such as tetramethoxysilane (TMOS) and tetraethoxysilane (TEOS) is

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irradiated with ultraviolet light, the organic group is released to cause

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decomposition and the silicon-oxygen bond portion can form bonding with an inorganic or organic material of various types, so that adhesion either to an inorganic material or an organic material can be attained by the alkoxide. The silicon alkoxide is ideally vitrified and becomes SiO_2, but from the standpoint of the object of the present invention, complete vitrification into SiO_2 is not necessarily required and the object can be achieved if necessary adhesion and UV transparency can be obtained. A metal alkoxide such as zirconium alkoxide, titanium alkoxide, yttrium alkoxide and germanium alkoxide, an alkoxide other than these, or a mixture thereof also undertakes the same reaction. The alkoxide group is not particularly limited and may be a monomer or may be in the form of an oligomer or a polymer. As for the production conditions, suitable conditions may be selected by taking account of the coatability and the size of decomposable volatile component (organic group).

In the present invention, vacuum ultraviolet light at a wavelength shorter than 200 nm is suitably used.

The light source of ultraviolet light for use in the present invention is not limited but examples thereof include a low-pressure mercury lamp, and an excimer lamp having a wavelength in the vicinity of 172 nm. Also, radiation light including undulator can be used. The light source is sufficient if it contains ultraviolet light. A laser light source may also be used.

At the time of irradiating ultraviolet light, an ultraviolet light-absorbing material, particularly oxygen, is contained in air and therefore, in view of irradiation efficiency, the ultraviolet light is preferably irradiated after the atmosphere surrounding

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the materials to be adhered is at least partially purged with nitrogen or rare gas, or in vacuum.

The conditions in irradiating ultraviolet light, such as wavelength, intensity, time period, atmosphere and temperature, may be appropriately selected but unlike the glass melt-adhesion method, high-temperature heating is not necessary in the present invention and the materials to be adhered (adhered materials) are advantageously free from thermal damage. For example, room temperature may be employed.

The method of adhering two materials by the present invention is described in greater detail below by referring to the drawings.

The method for adhering UV-transparent materials of the present invention can be used, for example, as shown in Figs. 1 and 2, for the adhesion of superposing and attaching two quartz glass bodies to each other; the adhesion of superposing and attaching main planes of two UV-transparent material plates to each other is apparently useful in practice, and various applications can be expected.

It is considered that the present invention is particularly useful for adhering two or more sheets of quartz glass in the lateral direction to prepare a larger area quartz glass plate and producing a product such that the enlarged area quartz glass plate is transparent to ultraviolet light.

For example, an excimer lamp is used in a light source apparatus for performing photo-cleaning (ultraviolet cleaning) in the process of producing a semiconductor but the excimer lamp must be placed in a nitrogen atmosphere and therefore, a quartz glass is used for the window of taking out light. In this case, the dimension of light source apparatus is restricted by the dimension of one sheet of quartz glass. However, when an adhered quartz glass having UV transparency produced by the present invention is used, the dimension is not

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restricted and a light source apparatus having a desired

size can be produced.

Furthermore, the adhering method of the present invention can be used for attaching five quartz glass plates with each other to produce a rectangular parallelopiped quartz glass cell for use in chemical analysis or the like, for producing a quartz glass instrument, or for adhering respective elements, for example, in the production of an optical part or in the attachment of lenses with each other.

Fig. 2 and Figs. 3A to 3F show an example of the above method of adhering two or more plate materials. In these Figures, 1a and 1b are a glass plate, 2 is a glass stacked body, 3 is an adhered part, 4 is a small plate for adhesion, 6 is a light source and 7 is ultraviolet light. Two glass plates 1a and 1b in various shapes may be adhered by placing these plates to face each other as shown in Figs. 3A to 3D, by superposing the edges as shown in Fig. 3E, or by using a small plate 4 for adhesion as shown in Fig. 3F.

Fundamentally, an alkoxide solution is dropped or coated on one or both of two materials, these materials are superposed or stringed and ultraviolet light is irradiated on the portion containing the alkoxide, or an alkoxide solution is injected into the space between two materials and ultraviolet light is irradiated on the portion containing the alkoxide, whereby the alkoxide can be vitrified and at the same time, caused to exert the adhesion effect and those two materials can be adhered (see Fig. 2).

It is preferred to have a step of previously polishing the portions corresponding to adhesion surfaces of two materials to smooth the surfaces.

In the adhesion process of the present invention, the portions corresponding to adhesion surfaces of two materials are more preferably cleaned so as to enhance the adhesive property.

In the adhesion process, a mechanical pressure is

applied to two materials from both sides during the irradiation of ultraviolet light on the portion containing the alkoxide, so as to enhance the adhesive property.

In the adhesive process, the ultraviolet light is preferably irradiated on two materials in a nitrogen gas or rare gas atmosphere so as to eliminate ultraviolet-absorbing molecules in air and use the ultraviolet light with good efficiency.

In this way, quartz glass plates are adhered in the lateral direction by using the adhering method of the present invention, whereby a larger-area quartz glass plate can be obtained. When the entire adhesion surfaces of quartz glass plates are adhered through SiO_2 by using the adhering method of the present invention, the adhered quartz glass plate exhibits remarkably higher adhesive strength than expected and the quartz glass plates are completely integrated with each other. This adhered quartz glass can be used as a completely one-sheet quartz glass plate without worrying about separation. When the adhered part is observed, it can be confirmed, for example, that the adhesion is formed throughout the adhesion surface, the adhesion is free of a gap (at least a void crossing over the adhesion surface is not present), and the adhered part is airtight.

Fig. 4 shows one example of an ultraviolet light source apparatus where the adhered large-area quartz glass plate 11 obtained as above by the present invention is used for the window of transmitting light emitted from ultraviolet light sources 12. The ultraviolet light source apparatus 10 of Fig. 4 is an embodiment of the photo-cleaning apparatus, where a material 14 to be cleaned is disposed, if desired, movably disposed, in a container 13 and ultraviolet light 15 is irradiated on the material 14 to be cleaned from the ultraviolet light sources 12 through the window of the large-area quartz glass plate 11, thereby photo-cleaning the material 14.

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In the photo-cleaning apparatus of the present invention, the window 11 can be large-sized because the quartz glass plates are adhered to have a larger area, and therefore, the material which can be photo-cleaned by one operation is substantially free of restriction in the size and can be made extremely large, so that the photo-cleaning efficiency can be greatly enhanced.

EXAMPLES:

The present invention is described below by referring to Examples, however, these Examples are merely one example for properly describing the invention and the present invention is not limited in any way by these Examples.

(Example 1)

As shown in Fig. 1, two square quartz glass plates 1a and 1b having a thickness of 1 mm and a one-side length of 2 cm were prepared. On one surface of each quartz glass plate, a drop of tetramethyloxysilane (TMOS) [components: TMOS monomer: 91.8%, TMOS oligomer: 3.4%, water/methanol: 4.8%] which is an alkoxide was dripped. Then, the surfaces wetted with TMOS of quartz glasses were superposed one on another and as shown in Fig. 2, ultraviolet light 7 having a peak at a wavelength of 172 nm was irradiated on the two-sheet quartz glass plate 2 from a xenon excimer lamp 6 for 60 minutes. At this time, the distance between the xenon excimer lamp 6 and the quartz glass plate 2 was 2 mm.

As a result, the two-sheet quartz glass plates 2 were firmly adhered. The adhered two-sheet quartz glass plates 2 were measured on the absorption spectrum in the ultraviolet region. Then, absorption was exhibited in the short wavelength region of 160 nm or less. This is an absorption inherent in the quartz glass. Thus, the adhered quartz glass 2 was verified to transmit the ultraviolet light down to a wavelength of 160 nm.

(Example 2)

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CLAIMS

1. (Amended) A method for adhering a transparent material, comprising interposing an alkoxide between two materials, at least one of which comprises a medium transparent to ultraviolet light, externally applying a mechanical pressure to said two materials so as to reduce uneven gaps and improve contact between said two materials, using a nitrogen or rare earth gas atmosphere in order to prevent ultraviolet absorption, and irradiating ultraviolet light with a wavelength shorter than 200 nm to the above alkoxide portion, thereby adhering those two materials.

2. (Amended) An adhered quartz glass plate comprising two or more quartz glass plates laterally adhered in accordance with the adhering method as set forth in claim 1 to provide a larger area, with the adhered part being transparent to ultraviolet light at a wavelength shorter than 350 nm.

3. (Amended) A photo-cleaning apparatus comprising a light source part having one or a plurality of excimer lamp(s) or low-pressure mercury lamp(s), by which ultraviolet light is irradiated from said light source to an article to be cleaned disposed in a cleaning chamber, characterized in that the adhered quartz glass plate as set forth in claim 2 is used for a window between the light source part and the cleaning chamber.